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Magnetic behaviour of europium ions in bismuth-borate glass matrix

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Glasses of the $xEu_2O_3 \cdot (100-x)[4Bi_2O_3 \cdot B_2O_3]$ system, with $0 \leq x \leq 40$ mol%, have been obtained and investigated by magnetic susceptibility measurements. Magnetic susceptibility data evidenced both Eu^{3+} and Eu^{2+} valence states as simultaneously present in the bismuth-borate glass matrix. These ions are involved in negative superexchange interactions, being antiferromagnetically coupled. The content of Eu^{3+} and Eu^{2+} ions was determined from the experimental values of the effective magnetic moments for all samples.

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1. Introduction

Glasses containing rare earth ions are the subject of a great deal of interest due to their important physical and chemical properties. Such glasses are heat and mechanically resistant, chemically stable and show interesting optical and magnetic properties [1]. Among them, glasses containing europium ions have attracted much attention due to their magnetic and optical properties, very promising for technological applications [2-11]. The information related to the magnetic interactions between the europium ions and in particular, to the magnetic ordering in these materials is also very interesting [2-11]. Thus, magnetic susceptibility measurements may give information concerning the presence of europium ions in different valence states, the amount of ions in each valence state as well as the type of the interactions between them [2-7].

In the previous papers [12,13] we have investigates the Erbium and Terbium in bismuthate glasses.

We considered the $4Bi_2O_3 \cdot B_2O_3$ glass matrix to be a very interesting host for the europium ions. In the present work we investigated the $xEu_2O_3 \cdot (100-x)[4Bi_2O_3 \cdot B_2O_3]$ vitreous system with $10 \leq x \leq 40$ mol% by magnetic susceptibility measurements, in order to obtain information concerning magnetic properties of these glasses.

2. Experimental

Glasses of the system $xEu_2O_3 \cdot (100-x)[4Bi_2O_3 \cdot B_2O_3]$ were prepared using reagent grade purity Bi_2O_3, H_3BO_3 and Eu_2O_3 in suitable proportion. The mechanically homogenized mixtures were melted in sintered corundum crucibles at 1100°C, in an electrical furnace. The samples were put into the electric furnace direct at this temperature. After 15 minutes, the molten material was quenched at room temperature by pouring onto a stainless–steel plate. The samples were analyzed by means of X-ray diffraction using a Bruker D8 ADVANCE X-ray. The pattern obtained did not reveal any crystalline phase in the samples up to 40 mol% Eu_2O_3.

Magnetic susceptibility measurements were performed on a Faraday-type balance in a magnetic field of 1T over the 80–300 K temperature range. The overall accuracy of the magnetic susceptibility measurements is estimated to be approximately 1% due to the uncertainty of the equipment calibration. Correction due to the diamagnetism of the Bi_2O_3, B_2O_3 and Eu_2O_3 were taken into account in order to obtain the real magnetic susceptibility of europium ions in the studied glasses.

3. Results and discussion

The temperature dependence of the reciprocal magnetic susceptibility shows a Curie-Weiss-type behaviour (Fig. 1), with negative paramagnetic Curie temperature for all studied glasses. This fact suggests the participation of europium ions (their proportion depends on x) at superexchange magnetic interactions, of antiferromagnetic type, in all studied concentration range. Due to the disordered structure of glasses, the magnetic order takes place at short range making possible a mictomagnetic-type order [14]. The peculiar structure specific to vitreous oxide solids impose the short-range character of magnetic interactions and enhance the structural image of clusters.

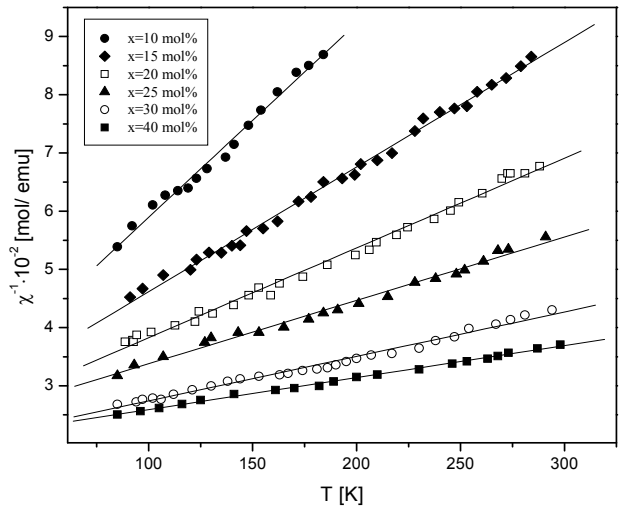

Fig. 1. Temperature dependence of the reciprocal magnetic susceptibility for $xEu_2O_3 \cdot (100-x)[4Bi_2O_3 \cdot B_2O_3]$ glasses.

The absolute magnitude of θ_p values increases with the Eu_2O_3 content for the studied glasses (Fig. 2) and denotes the intensification of the exchange interactions as the concentration of the europium ions rises [15].

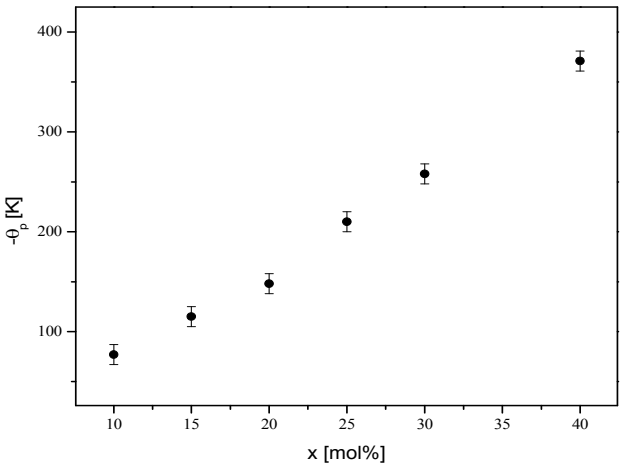

Fig. 2. The composition dependence of the paramagnetic Curie temperature for $xEu_2O_3 \cdot (100-x)[4Bi_2O_3 \cdot B_2O_3]$ glasses.

The composition dependences of the molar Curie constant (C_M) and of the effective magnetic moment (μ_{eff}) are presented in Table 1. For all the glasses experimental values obtained for C_M and consequently for μ_{eff} are higher than those which correspond to the Eu_2O_3 content, considering that all europium ions are in Eu^{3+} valence state, but they are lower than those calculated for the case when all europium ions would be Eu^{2+} species (Table 1). Therefore we consider that in these glasses are present both Eu^{3+} and Eu^{2+} ions. The presence of Eu^{3+} and Eu^{2+} ions has been evidenced in other oxide glasses, too [2-7]. Having in view this supposition and using the atomic magnetic moment values of free Eu^{3+} and Eu^{2+} ions: $\mu_{Eu^{3+}} = 3.40\,\mu_B$ and $\mu_{Eu^{2+}} = 7.12\,\mu_B$ [2], we can estimate in first approximation the molar fraction of these ions in the investigated glasses using the relations:

$$x \cdot \mu_{eff}^2 = x_1 \cdot \mu_{Eu^{3+}}^2 + x_2 \cdot \mu_{Eu^{2+}}^2, \quad x = x_1 + x_2,$$

where μ_{eff} represents the experimental effective magnetic moment value (Table 1) determined from the temperature variation of the reciprocal magnetic susceptibility (Fig. 1), while x_1 and x_2 are the molar fractions of Eu^{3+} and Eu^{2+} ions. The results obtained are listed in Table 1.

From these data one remarks that the molar fraction of both Eu^{3+} and Eu^{2+} ions increases in the whole studied concentration range, the molar fraction of Eu^{3+} ions being higher than that of the Eu^{2+} ions.

Table 1. Molar Curie constant, experimental values of μ_{eff} and molar fraction of Eu^{3+} (x_1) and Eu^{2+} (x_2) ions for $xEu_2O_3 \cdot (100-x)[4Bi_2O_3 \cdot B_2O_3]$ glasses.

x [mol%]	C_M [$\pm 1\times10^{-4}$ emu K/ mol]	μ_{eff} [$\pm 1\times10^{-2}$ μ_B]	x_1 [mol%]	x_2 [mol%]
10	0.3004	3.46	9.9	0.1
15	0.4667	3.52	14.7	0.3
20	0.6487	3.60	19.3	0.7
25	0.9186	3.83	23.0	2.0
30	1.3088	4.17	25.5	4.5
40	1.8185	4.26	33.3	6.7

4. Conclusions

Glasses of the $xEu_2O_3 \cdot (100-x)[4Bi_2O_3 \cdot B_2O_3]$ system were obtained within a large concentration range, i.e. $0 \le x \le 40$ mol%. The magnetic susceptibility data revealed superexchange-magnetic interactions involving europium ions, antiferromagnetically coupled. Europium ions enters the $4Bi_2O_3 \cdot B_2O_3$ glass matrix in both Eu^{3+} and Eu^{2+} valence states, the first being dominate.

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